



Heat-treated metal phthalocyanine complex as an oxygen reduction catalyst for non-aqueous electrolyte Li/air batteries

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ABSTRACT

In this work we study heat-treated FeCu-phthalocyanine (FeCuPc) complexes as the catalyst for oxygen reduction in non-aqueous electrolyte Li/air cells by supporting the catalyst on a high surface area Ketjenblack EC-600JD carbon black. It is shown that the resultant FeCu/C catalyst not only accelerates the two-electron reduction of oxygen as " $O_2 + 2Li^+ + 2e \rightarrow Li_2O_2$ ", but also catalyzes the chemical disproportionation of Li_2O_2 as " $2Li_2O_2 \rightarrow 2Li_2O + O_2$ ". In Li/air cells, the catalyst reduces polarization on discharge while simultaneously reducing the fraction of Li_2O_2 in the final discharged products. In a 0.2 mol kg^{-1} $LiSO_3CF_3$ 7:3 (wt.) propylene carbonate (PC)/tris(2,2,2-trifluoroethyl) phosphate (TFP) electrolyte, the Li/air cells with FeCu/C show at least 0.2 V higher discharge voltage at 0.2 mA cm^{-2} than those with pristine carbon. By measuring the charge-transfer resistance (R_{ct}) of Li/air cells at temperatures ranging between -30°C and 30°C , we determine the apparent activation energy of the discharge of Li/air cells and discuss the effect of FeCu/C catalyst on the oxygen reduction in Li/air cells.

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1. Introduction

Li/air batteries are more complicated than the traditional metal/air batteries since their discharge products (Li_2O_2 and Li_2O) are insoluble in non-aqueous electrolytes. During discharge, the Li_2O_2 and Li_2O deposit and accumulate on the surfaces of a carbon air cathode, which eventually blocks the access of oxygen to catalytic sites and halts the operation of the battery. Therefore, the amount that the carbon air cathode can accommodate for the discharge products determines the specific capacity of Li/air cells [1–3]. To achieve high specific capacity, a liquid/solid two-phase reaction zone between the liquid electrolyte and solid catalytic sites is required for the Li/air cells to achieve the maximum reaction area and the largest accommodation capacity [3]. However, such cells are intrinsically low power since diffusion of the dissolved oxygen in liquid electrolyte is slow and the discharge products cannot be removed from the catalytic sites. For these low power Li/air cells, the pristine carbon without any other catalysts has been directly used as the catalyst for the oxygen reduction [2–8].

Catalytic reduction of oxygen in Li/air battery takes place through such three steps as: (1) dissolution of oxygen from gas phase into liquid electrolyte, (2) diffusion of the dissolved oxygen into catalytic sites on the carbon surface, and (3) catalytic reduction of oxygen into Li_2O_2 or Li_2O . Of them, the last step might become

the rate-determining step to limit the discharge performance of Li/air cells when the discharge current rate is increased. Therefore, more effective catalysts are needed to increase the power capability of Li/air cells. Transition metal N_4 -macrocycle complexes have long been known to be highly active for the catalytic reduction of oxygen. However, these compounds are either soluble or chemically instable in aqueous acidic or alkaline electrolyte solutions. For these reasons, the technique of heat-treatment with carbon has been used to enhance catalytic activity and increase chemical stability against the aqueous electrolyte environments [9–11]. The heat-treated transition metal N_4 -macrocycle complexes have been considered as an excellent catalyst for the oxygen reduction in alkaline metal/air cells and fuel cells [9–15]. Keeping this knowledge in mind, in this work we study the effect of oxygen reduction catalyst on the discharge performance of Li/air cells by selecting a heat-treated iron and copper phthalocyanine (FeCuPc) complex as the catalyst and loading it onto a high surface area Ketjenblack EC-600JD carbon black.

2. Experimental

Ketjenblack EC-600JD carbon black (AkzoNobel) was used as the control and supporting carbon for catalyst. FeCu/C catalyst was received from Acta S.p.A, Italy, which was prepared by first absorbing a FeCuPc complex solution onto Ketjenblack EC-600JD carbon black and then heating the mixture at temperatures between 800°C and 900°C in an argon atmosphere. The final FeCu/C catalyst contained 1.5 wt.% Fe and 1.7 wt.% Cu, respectively, which corresponds

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to a 1:1 molar ratio of Fe to Cu. In this work we referred to the FeCu/C catalyst as a composite of the Ketjenblack carbon and FeCuPc pyrolytic products. Using the carbon materials above, air electrodes with a composition of 90 wt.% carbon and 10 wt.% polytetrafluoroethylene (PTFE) were prepared by mixing calculated amounts of carbon and PTFE emulsion (Teflon[®], solid content = 61.5%, DuPont Co.) and rolling the mixed paste to form a free-standing cathode sheet. The resultant air cathode sheet, equaling to a total 2.88 wt.% of metal (Fe and Cu) content, was punched into small disks with an area of 0.97 cm² and dried at 100 °C under vacuum for at least 8 h.

A 0.2 mol kg⁻¹ (m) LiSO₃CF₃ 7:3 by weight propylene carbonate (PC)/tris(2,2,2-trifluoroethyl) phosphate (TFP) electrolyte was prepared in an argon-filled glove-box by mixing calculated amounts of LiSO₃CF₃ (96%, Aldrich), PC (Ferro) and TFP, in which the TFP was synthesized in-house as described in Ref. [16]. This electrolyte was selected as it is superior to other carbonate-based electrolytes in both the dissolution kinetics and the solubility of oxygen [17,18]. In a dry-room having a dew point of below -90 °C, Li/air cells with an air window of 0.97 cm² were assembled by stacking a Li foil, a Celgard[®] 3500 membrane, a carbon air cathode, a Ni mesh as the current collector, and an air window in sequence into a coin cell cap. To activate the cell, 200 µL of liquid electrolyte was added through the air-window, followed by applying a vacuum for 20 s to ensure complete wetting. Extra liquid electrolyte was removed by gently wiping a filter paper on the top of the Ni mesh. The electrolyte-activated cell was clamped on a cell holder to test as a Li/air cell. The same procedures were followed to assemble three-electrode cells except for using two pieces of separators and sandwiching a small piece of Li foil as the reference electrode between these two separators. Detailed descriptions on the cell configuration and assembly procedure can be found in Ref. [3].

An Arbin BT-2000 cyclizer was used for the discharge testing with a 1.5 V cutoff voltage. Specific capacity of the cells was calculated with reference to the weight of carbon in the air cathode. A Solartron SI 1287 Electrochemical Interface and a SI 1260 Impedance/Gain-Phase Analyzer were used for cyclic voltammetry, polarization, and impedance measurements. Impedance spectra of the cells were measured at open-circuit voltage (OCV) in frequencies ranging from 0.01 Hz to 10⁶ Hz by applying an ac perturbation of 0.10 mV in amplitude. Since the impedances of Li/air cells are highly dependent of the depth-of-discharge (DOD) [3], the cells were discharged to the same DOD for each comparison of the electrochemical properties. The conditions for other tests are described either in discussion or in related figure captions. Before each test, the cells rested for 2 h to reach equilibrium of oxygen concentrations between the air cathode (catalytic sites) and the air environment. Unless noted otherwise, the tests were carried out in the dry room and at room temperature (22 °C).

3. Results and discussion

3.1. Air cathode structure and Li/air cell's OCV

Ketjenblack EC-600JD is a highly branched carbon black consisting of 30–100 nm long aggregates [19]. After loading with catalyst, the surface area and pore volume of the carbon are significantly reduced as shown in Table 1. This is because many of pores in Ketjenblack carbon were filled with the thermal decomposition products of FeCuPc, including metal oxides and pyrolytic carbon [20]. Therefore, the FeCu/C air cathode has much lower pore volume than the pristine carbon air cathode.

It is interesting to note that all newly assembled Li/air cells with FeCu/C have constantly about 0.3 V higher OCV than those with the pristine carbon. The FeCu/C cells have an OCV ranging between 3.35 V and 3.50 V, which are even higher than the theoretical OCV

Table 1

Physical properties of carbon materials, air cathodes, and Li/air cells.

| | Ketjenblack EC-600JD | CuFe/C |
|---|----------------------|-------------|
| BET surface (m ² g ⁻¹) | 1413 | 751 |
| Pore volume (cm ³ g ⁻¹) | 2.06 | 1.23 |
| Electrode pore volume ^a (cm ³ g ⁻¹) | 5.46 | 3.64 |
| Li/air cell | Control cell | CuFe/C cell |
| Cell OCV (V) | 2.9166 | 3.331 |
| Cell impedance (Ω) | 270 | 226 |

^a Calculated by the solvent absorption method as described in Ref. [3].

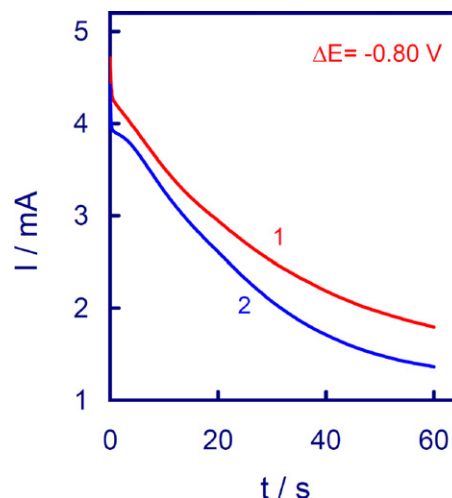
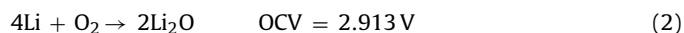
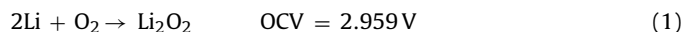


Fig. 1. Current–time response of Li/air cells when a -0.8 V of constant potential was applied to the OCV of the cell. (1) Control cell with pristine carbon, and (2) Li/air cell with FeCu/C.

based on the following reactions [21]:



This phenomenon can be explained by the chemical structure of FeCu/C catalyst. Many publications have reported that the final chemical components of the heat-treated transition metal N₄-macrocyclic complexes depend on the temperature of heating-treatment [11–15]. The most acceptable conclusion is that the complex forms MN₄ molecular moieties (where M represents a transition metal) at temperatures of 500–700 °C, it further loses nitrogen to form MN₂/MO mixtures at temperatures of 700–800 °C by combining oxygen atoms from the functional groups of the carbon edges, and finally converts all MN₂ into MO at even higher temperatures. Since the present FeCu/C was made at 800–900 °C, we consider that the Fe and Cu in the catalyst are present mainly in the form of metal oxides.

Based on the facts described above, we believe that the unusually high OCV of the FeCu/C based Li/air cells is due to the metal oxides, rather than the O₂ from air. To support our hypothesis, we conducted a polarization experiment on two Li/air cells having the same depth-of-discharge (DOD). The OCV and overall impedance of these two cells are listed in Table 1, and the polarization curves of these two cells with a -0.8 V constant potential applied to the OCV are compared in Fig. 1. It is shown in Table 1 that the FeCu/C cell has lower impedance than the control cell (i.e., 226 vs. 270 Ω). On contrary, the FeCu/C cell has lower current in the I–t response curve as indicated in Fig. 1, which disagrees with the ohmic rule. This confliction suggests that the initial OCV of the FeCu/C cell corresponds neither to reaction (1) nor to reaction (2), instead it reflects the OCV of the metal oxides themselves. The initial OCV ranging

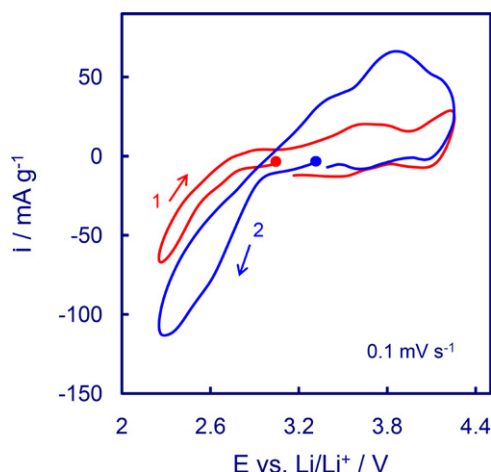


Fig. 2. Cyclic voltammogram of the first cycle of newly assembled Li/air cells. (1) Control cell with pristine carbon, and (2) Li/air cell with FeCu/C. Experiment conditions: the test was performed on a three-electrode cell between 2.2 V and 4.3 V at a potential scanning rate of 0.1 mV s^{-1} . The potential scanning started from cell's OCV as indicated by the solid dots in the figure, first downward to low potential and then upward to high potential.

between 3.35 V and 3.50 V of the FeCu/C cells is in agreement with those observed from the Li/CuO and Li/Fe₂O₃ cells [22,23].

3.2. Cyclic voltammogram of Li/air cells

Fig. 2 compares cyclic voltammograms of the first cycle of two Li/air cells. It is shown that the reduction of oxygen starts at 2.94 V vs. Li/Li⁺ in the FeCu/C cell, while at 2.80 V in the control cell. This oxygen reduction corresponds to reaction (1) and the 0.14 V higher shift in the reduction potential is attributed to the catalytic effect of FeCu/C. Furthermore, the FeCu/C cell shows much higher reduction currents than the control cell. This fact reveals that the FeCu/C catalyst reduces polarization in the Li/air cell. It appears that the FeCu/C also catalyzes the oxidation of Li₂O₂, i.e., the reversal of reaction (1), as indicated by a broad oxidation current peak at $\sim 3.8 \text{ V}$ vs. Li/Li⁺ when the potential is scanned back from 2.2 V. In the control cell, the similar oxidation peak seems not to appear until the potential is increased to 4.1 V. In addition, the control cell shows a pair of somehow reversible current peaks between 3.3 V and 3.9 V. These currents may be associated with the oxygen radical intermediates formed during the oxidation of Li₂O₂, which are considered to be responsible for the decomposition of carbonate solvents [24,25].

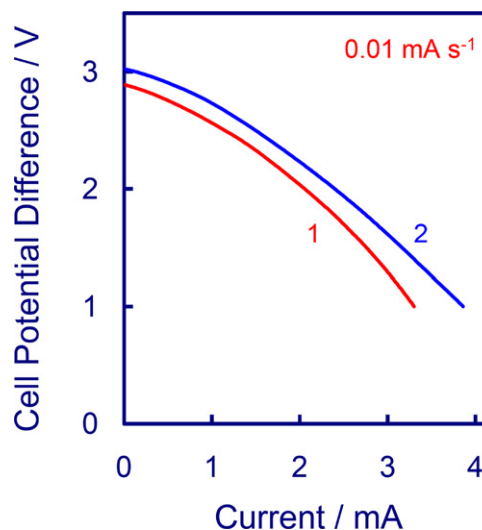


Fig. 4. Dynamic polarization of Li/air cells at 0.01 mA s^{-1} . (1) Control cell with pristine carbon, and (2) Li/air cell with FeCu/C.

3.3. Discharge characteristic of Li/air cells

Fig. 3 shows the effect of FeCu/C catalyst on the discharge performance of Li/air cells. In consecutive discharge (Fig. 3a), the FeCu/C cell shows about 0.2 V higher voltage than the control cell. This observation agrees with the cyclic voltammetric results as discussed in Fig. 2, and it is attributed to the reduced polarization by FeCu/C catalyst. Another significant difference in the voltage curves between two cells is that the catalyzed cell exhibits a second voltage plateau starting at $\sim 1.7 \text{ V}$. In early work [20], we have concluded that this second voltage plateau is due to the catalyst-induced solvent decomposition. If subtracting the capacity of the second voltage plateau, we can find that the specific capacity of the FeCu/C cell is a little lower than the control cell. This result agrees with the fact that the FeCu/C has less pore volume than the pristine carbon as indicated in Table 1.

Similar results are observed from intermittent discharge except that the specific capacities are significantly higher than those obtained from the consecutive discharge (compare Fig. 3a and b). The reason for this phenomenon is understandable since in intermittent discharge the rest between two discharges allows more oxygen to diffuse into the catalytic sites. On the other hand, the catalytic effect of FeCu/C on the oxygen reduction in Li/air cells also can be verified by the dynamic polarization experiment (see Fig. 4). In whole tested current range, the FeCu/C cell outperforms the control cell and the improvement seems to increase with the current.

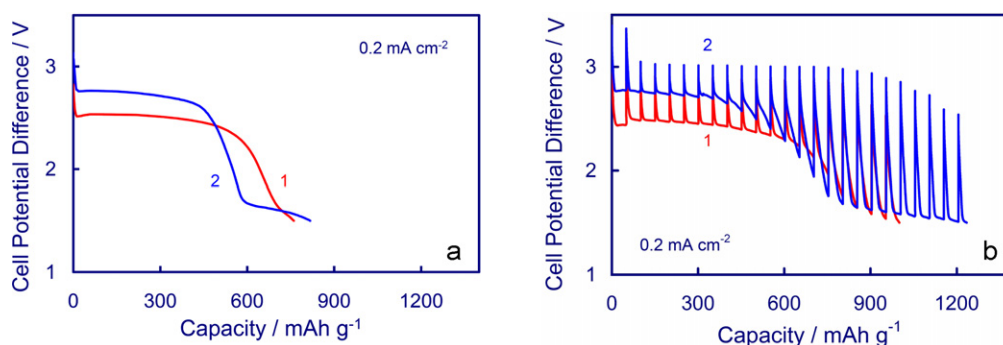


Fig. 3. Discharge characteristic of Li/air cells in a (a) consecutive discharge and (b) intermittent discharge. (1) Control cell with pristine carbon, and (2) Li/air cell with FeCu/C. Experiment conditions: both discharges used a 0.2 mA cm^{-2} current density. In intermittent discharge, the cell rested for 2 h after every 50 mAh g^{-1} discharge.

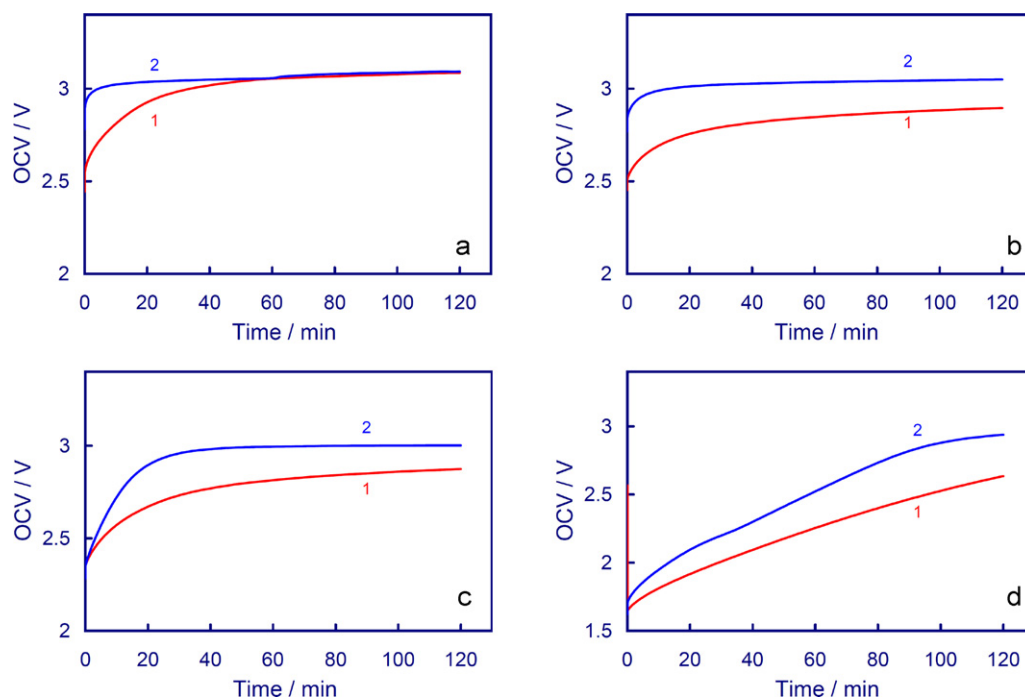


Fig. 5. OCV recovery of Li/air cells at different depth-of-discharge. (a) At 50 mA h g⁻¹, (b) at 300 mA h g⁻¹, (c) at 600 mA h g⁻¹, and (d) at 900 mA h g⁻¹. (1) Control cell with pristine carbon, and (2) Li/air cell with FeCu/C.

3.4. Role of FeCu/C catalyst in OCV recovery

Fig. 5a–d compares OCV recovery of two Li/air cells at different DOD. A general trend is that the OCV recovery slows down with an increase in the DOD. This is because the insoluble and non-conductive discharge products (Li₂O₂ and Li₂O) deposit on the carbon surface, which forms a passivation layer to suppress the diffusion of oxygen into the catalytic sites. For a cell with high DOD, longer time is required for the diffusion of oxygen into the catalytic sites since the passivation layer grows with DOD and since the OCV cannot get stable until the equilibrium of oxygen concentrations between the air cathode (catalytic sites) and the electrolyte is achieved. Fig. 5b–d indicates that a 2 h rest is not sufficient for the full OCV recovery although these cells eventually can recover to almost same OCV (~3.0 V), as represented by reaction (1) (not shown in Fig. 5).

Another interesting phenomenon is that the FeCu/C cell shows faster OCV recovery than the control cell. To understand this, we conducted the following two experiments:

1. Discharge two cells with pristine carbon and FeCu/C, respectively, to the same capacity, and then dip the discharged air cathodes into 1 mL deionized water. In this process, the Li₂O₂ formed in discharging was reacted with water to form H₂O₂ and LiOH. Upon the end of reaction, the same amount of KMnO₄/H₂SO₄ solution was added into the clear solution to roughly determine the amount of H₂O₂. As a result, we found that the color of KMnO₄ disappeared immediately in the solution with pristine carbon, while that in the solution with FeCu/C decolorized slowly and the color could not disappear completely even in the end. These results indicate that in the same capacities the FeCu/C cell produces less Li₂O₂ as compared with the pristine carbon cell.
2. Dissolve small amount of commercial Li₂O₂ powder into deionized water. When the Li₂O₂ was completely dissolved to form H₂O₂, the clear solution was split into two parts, to which small amount of pristine Ketjenblack EC-600JD carbon black and

FeCu/C powder, respectively, was added. As a result, the FeCu/C powder caused violent decomposition of H₂O₂ accompanied by numerous oxygen bubbles, while the pristine carbon caused no change.

The above two experiments suggest that the FeCu/C also catalyze the chemical disproportionation of Li₂O₂ as:



The faster OCV recovery of FeCu/C cell in Fig. 5a–d can be well explained by reaction (3) as follows: when the discharge is halted, the Li₂O₂ in contact with the FeCu/C catalytic sites undergoes reaction (3) to release O₂. Since the reaction occurs right on the Li₂O₂/catalyst interface, the released O₂ can be immediately utilized to establish the equilibrium of oxygen concentrations between the catalytic sites and the electrolyte, which results in a faster OCV recovery. On the other hand, the faster OCV recovery of the FeCu/C cell suggests that the FeCu/C catalyst might not affect the further reduction of Li₂O₂ as shown by reaction below:



The discussion above indicates that the FeCu/C not only accelerates the two-electron transfer reaction (1), but also catalyzes the non-redox reaction (3). Since the latter is a solid/solid two-phase reaction that only can occur in the interface between the catalyst sites and Li₂O₂ phase, the catalytic activity of FeCu/C on reaction (3) is not as effective as on reaction (1). Due to the catalytic effect on reaction (3) and the difficulty in oxidizing electrochemically Li₂O to Li₂O₂ and oxygen, the FeCu/C catalyst may not be a good choice for the catalyst of rechargeable Li/air batteries.

3.5. Impedance analysis on Li/air cells

In previous work [3], we have shown that the impedance of a Li/air cell is changed greatly with the cell's DOD. Therefore, in the present work two identical Li/air cells were assembled and discharged to the same DOD, followed by measuring impedance

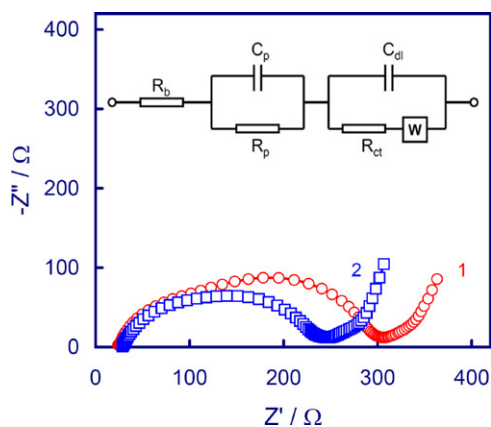


Fig. 6. Impedance spectra of Li/air cells, in which two cells are identical in the size and weight of the air cathode and in the cell's DOD (100 mA h g^{-1}). (1) Control cell with pristine carbon, and (2) Li/air cell with FeCu/C.

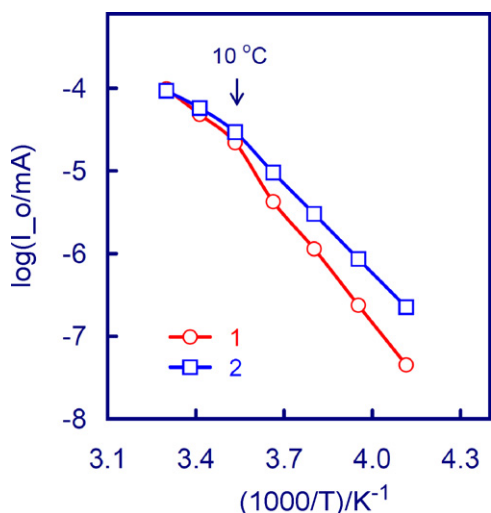


Fig. 7. Arrhenius plot of the exchange current of Li/air cells. (1) Control cell with pristine carbon, and (2) Li/air cell with FeCu/C.

to examine the effect of FeCu/C catalyst on the oxygen reduction. Fig. 6 shows impedance spectra of two cells measured at a DOD of 100 mA h g^{-1} . It is shown that the impedance spectra contain two overlapped semicircles, in which the semicircle at high frequencies relates to the discharged product layer and that at low frequencies corresponds to the charge transfer of cell reaction. Therefore, an equivalent circuit as shown in the inset can be used to fit the electrical elements of the impedance spectra. Since the diameter of the semicircle at low frequencies corresponds to the charge-transfer resistance (R_{ct}) of the cell reaction [26,27], the exchange current (i_o) of the Li/air cells can be calculated using equation below [28]:

$$i_o = \left(\frac{RT}{nF} \right) \frac{1}{R_{ct}} \quad (5)$$

where R is the gas constant, F is the Faraday constant, and T is the temperature. Arrhenius plots of the exchange currents for two cells are shown in Fig. 7, from which the apparent activation energy of the Li/air cells is estimated as follow: at temperatures above 10°C , the apparent activation energy is 50.2 kJ mol^{-1} for the control cell

and 41.4 kJ mol^{-1} for the FeCu/C cell. At temperatures below 10°C , the apparent activation energy is 86.1 kJ mol^{-1} for the control cell and 69.1 kJ mol^{-1} for the FeCu/C cell. These results indicate that the FeCu/C catalyst can effectively reduce the apparent activation energy of Li/air cells.

4. Conclusions

Based on the results of this work, the following conclusions can be made: (1) the unusually high OCV of the newly assembled Li/air cells with FeCu/C catalyst corresponds to the OCV of catalyst itself, rather than to the oxygen reduction, (2) the FeCu/C catalyst not only accelerates the two-electron oxygen reduction, but also catalyzes the non-redox Li_2O_2 disproportionation. In Li/air cells, the former reduces cell's polarization and the latter increases OCV recovery rate, (3) since the catalytic disproportionation of Li_2O_2 is a solid/solid two-phase reaction occurring in the interface between the catalytic sites and Li_2O_2 particles, the catalytic effect of FeCu/C on it is not as effective as on the two-electron oxygen reduction, and (4) the FeCu/C catalyst can effectively reduce the apparent activation energy for the discharge of Li/air cells.

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